SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

QUARTERLY REPORT NO. 6

PERIOD COVERED: February 1, 1967 -
                  April 30, 1967

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TECHNICAL CONTENT STATEMENT

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I   OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics
Operations Division has agreed to provide, on a level of
effort basis, between 100.8 and 106.8 direct man months of
effort to assist the Jet Propulsion Laboratory in the
development of a new or improved polymeric binder for
advanced solid propellant and hybrid solid grains. The
detailed objectives are described in Quarterly Report No. 1.

II.   ABSTRACT

Several chain transfer agents are being investi-
gated as to their suitability for placing desirable
functional groups at the ends of ethylene-neohexene copolymer
chains. Symmetrical disulfides, such as dimethyl dithio-
glycolate were not very effective as telogens for ethylene/
neohexene copolymers. Much more promising results have been
obtained with telogens containing the carbon-halogen bond.
Carbon tetrachloride gave telomers containing $-Cl$ and $-CCl_3$
as polymer end groups. Conversion of these groups to $-COOH$
has proven to be unexpectedly difficult. In order to
circumvent these problems telomers have been made containing
more reactive end groups. The telogens presently under
investigation are bromotrichloromethane ($BrCCl_3$), bromoacetic
acid (BAA), α-bromoisobutyric acid (BIBA), and t-butyl
α-bromoisobutyrate (BBIB).

Telomers have been obtained from each of these
telogens, and the analytical data thus far received are
quite favorable. In particular, the first BBIB telomer
analysed contains .95 ester groups and .84 bromine atoms
per molecule.

These products should be easier to convert to
difunctional carboxyl terminated prepolymers than any
products produced to date. Having one COOH group per molecule
as a starting point, we plan to use the more reactive bromide
group in various ways to obtain additional carboxylic acid
functionality.

Model compound studies on 11-bromohendecanoic
acid have demonstrated the feasibility of this approach for
preparing dicarboxylic acids.

III. SCOPE OF PROJECT

The scope of this work has not changed from the program outlined in the work statement. The experimental program is directed toward improving the functionality of the prepolymer.

IV. INTRODUCTION

In our fifth quarterly report we described ethylene-neohexene copolymerizations which were carried out in a continuous, high pressure tube reactor. It was demonstrated that prepolymers having the desired ethylene/neohexene combined ratio and molecular weight could be made with ease. The carboxyl functionality of these polymers was closer to one than two, which was found to be due to disproportionation of radicals from the initiator, DMAB. It was concluded that azodicarboxylic acid ester initiators should only be used in low concentrations for initiation purposes, and that terminating agents should be chosen which will not disproportionate or act as hydrogen transfer agents.

These considerations led to the decision to investigate the use of telomerizing agents which would, by the process of chain transfer, place useful functional groups at each end of each molecule. Two classes of compounds were chosen for initial examination, symmetrical disulfides, and molecules containing the carbon-halogen linkage. Three symmetrical disulfides were synthesized for use as chain transfer agents. These were, dimethyl ν,ν'-dithio dibutyrate, di-t-butyl α, α' dithio bis [isobutyrate] and dimethyl dithio glycolate. Carbon tetrachloride was chosen as the first telogen containing the carbon-halogen bond. Ethylene-neohexene copolymers were made in the presence of CCl_4 and found to be terminated at one end with -Cl and at the other with $-CCl_3$, as expected.

The report which follows describes the efforts which have been made to convert the CCl_4 telomers into polymers having COOH termination. Further evolution and extension of this concept to telomers made with $Br-CCl_3$, $\alpha-$ bromo isobutyric acid and similar telogens is also covered. Our evaluation of symmetrical disulfides as telogens has been completed and is also described below.

V.   TECHNICAL DISCUSSION

A.   Preparation of Ethylene-Neohexene Telomers Using CCl$_4$ as Telogen

In our last quarterly report we discussed the use of carbon tetrachloride as a telogen. When present in a polymerization reaction mixture, carbon tetrachloride participates in chain transfer reactions which lead to polymer structures having a trichloromethyl group upon one end of each chain and a chloride upon the other end. We also reported the results of four such telomerizations run in the small stirred autoclave at 90°C (runs 23 EMS-63, 64, 65 and 90). In the past quarter we have carried out further telomerizations using CCl$_4$ in both the stirred autoclave and the continuous tubular reactor. The results of the two stirred autoclave runs are summarized in Table I.

Runs 126 and 128 were made at a temperature of 160°C using di-tertiary butyl peroxide (DTBP) as the free radical initiator. These runs were pilot studies to determine approximate conditions to use in the tubular reactor runs. At the higher temperatures required for efficient operation of a tubular reactor, neither DMAB nor AIBN would be suitable initiators. Comparing Run 126 with Run 90 (reported last quarter), which also has a CCl$_4$/Monomer ratio of .003, one notes an increased yield and a decreased viscosity for the product prepared at 160°C. These changes are due to the increased polymerization rate and the greater chain transfer activity of CCl$_4$ at the higher temperature. We cannot evaluate the functionality of the product from Run 126 as yet, however, because of the inconsistencies in the analytical data received on this run (the elemental analyses on C, H, Cl, and O added up to 92%; 1300 molecular weight does not fit the viscosity data at all). The sample has been resubmitted for analysis.

Run 128, in which a larger CCl$_4$/Monomer ratio (.006) was used, gave a product with a lower molecular weight. The analytical data indicate that this telomer contains 1.69 chlorine functional groups (Cl-C- as well as -CCl$_3$) per molecule.

In our last quarterly report, we outlined the procedure used in making ethylene-neohexene copolymers in the tubular reactor using DMAB initiator. Essentially the same procedure was used to prepare the CCl$_4$ telomers with the

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TABLE I

STIRRED AUTOCLAVE RUNS

CCl$_4$ TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

Run No. 23-EMS	126	128
CHARGE:		
Solvent	---	---
Solvent Wt. gms.	---	---
Initiator	DTBP	DTBP
Initiator Wt. gms.	.5	.5
Carbon Tetrachloride, gms.	8	16
Neohexene, gms.	690	686
Ethylene, gms.	255	254
Mol. Ratio S/M, CCl$_4$ to Monomers	.003	.006
REACTION CONDITIONS:		
Temperature, °C	160	160
Pressures psi		
Initial	15000	15000
Final	14000	14000
Reaction time, hrs.	.17	1.0
PRODUCTIVITY:		
Yield, gms.	85	68
Conversion, %	9.0	7.2
Rate, % per hr.	52.9	7.2
PHYSICAL PROPERTIES:		
Molecular Weight	1300*	587
Brookfield Viscosity, cps.	15,400	650
Specific Viscosity, 80°C	.031	.019
Carbon, Wt. %	78.79*	68.47
Hydrogen, Wt. %	13.46*	11.37
Oxygen, Wt. %	0.00*	.17
Chlorine, Wt. %	0.27*	20.36
FUNCTIONALITY:		
Chlorine (Cl$_2$/mol.)	?	1.69
Oxygen (O$_2$/mol.)	?	.06

DESCRIPTION: Colorless, Slightly
                                                        Hazy Oils

* Analytical Results Questioned
  Sample Resubmitted

exception that in some of the runs a "split feed" was used. The split feed allows one to maintain a more nearly uniform level of telogen and initiator throughout the length of the tubular reactor. This is accomplished by injecting fresh initiator and telogen into the polymerization mixture midway along the reactor. In the cases where split feed was used, an inert solvent, iso-octane, was used to convey a dilute solution of DTBP and CCl_4 into the reactor's secondary feed. The primary feed mixture was a solution of ethylene, CCl_4, and DTBP in neohexene. No added solvent was used in the primary feed.

All of the CCl_4 telomerization products from the tubular reactor were stripped to 155°C at 2 mm, and one drop of stabilizer, dibutyl tin dilaurate, was added prior to stripping to minimize dehydrohalogenation. A distillate fraction, very likely low molecular weight telomers with CCl_4, was obtained between 120°C @ 300 mm to 155°C @ 2 mm. This fraction varied between 9 to 20 weight per cent of the total product. It was not included in conversion calculations.

The results of these tubular reactor runs without split feed are given in Table II.

With the exception of Runs 10 and 12 where t-butyl peroxypivalate (TBPP) was used, di-t- butyl peroxide (DTBP) was used in all of the runs.

In our first run in the tubular reactor the jacket temperature was 220°C. This is the temperature such that 95 per cent of the di-t-butyl peroxide (DTBP) is consumed at a residence time of 60 seconds, providing incoming feed is at 200°C. Two tubes were used, one as a preheater for the first two runs. At 220°C, very low Brookfield viscosity product was made with evidence of dehydrochlorination (dark color). Jacket temperature was reduced to 200°C and the color improved with a threefold increase in Brookfield viscosity.

The molecular weight of this product was 667. Dropping the temperature to 180°C, and increasing residence time to three minutes doubled the Brookfield viscosity to 2,200 cps. However, the molecular weight was a bit low (767). From these first five experiments it was obvious that either lower temperatures, lower telogen concentration or both would have to be used to obtain a higher molecular weight.

TABLE II

TUBULAR REACTOR RUNS - NO SPLIT FEED

CC14 TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

Run No 24 EMS	2	4	6	8	10	12	14
FEED COMPOSITION							
Neohexene, Wt. %	72.4	↑	↑	↑	↑	72.6	72.8
Ethylene, Wt. %	26.8	↑	↑	↑	↑	26.9	26.9
CC14. Wt. %	0.71	↑	↑	↑	↑	.24	.28
CC14, Mole Ratio	.0022	↑	↑	↑	↑	.0007	.001
Initiator	DTBP	↑	↑	↑	TBPP	TBPP	DTBP
Initiator, Wt. %	0.05	↑	↑	↑	.079	.187	.05
Total Feed, gms.	7552	7630	7551	6717	7419	3582	7430
REACTION CONDITIONS							
Temperature, °C							
Jacket	225	203	180	180	160	160	180
Internal, max.	222	183	166	166	140	147	165
Pressure, mpsi	20±2.5	30±2.5	↑	↑	↑	↑	↑
Operating Time, hrs.	3.42	3.35	3.27	2.90	3.25	1.55	3.1
Nominal Hold-up Time, min.	0.99	.96	2.83	2.83	0.95	0.94	2.73
Number of Tubes	2	2	4	4	2	2	4
PRODUCTIVITY							
Yield, gms.	242	304	300	277	128	114	203
% Conversion	3.2	4.0	4.0	4.2	1.7	3.2	2.8
Production Rate, gms./hr.	70.9	90.6	91.8	95.5	39.4	73.5	65.5
PHYSICAL PROPERTIES							
Molecular Wt.	516	667	767	747	649	1114	1009
Brookfield Visc., cps.	436	1212	2194	2276	1350	25,100	11,000
Specific Visc. @ 80°C	.013	.016	.021	.022	.018	.028	.024
Wt. % Cl	11.61	11.48	12.32	11.91	17.58	6.20	6.51
Wt. % O	.3	.27	0.0	0.0	.17	.17	.19
Description	dark	hazy	straw oil				↑
FUNCTIONALITY							
Cl2 per molecule	.85	1.08	1.33	1.25	1.61	.97	.93
O2 per molecule	.09	.11	0.0	0.0	.07	.12	.12

The next run was made at 160°C using t-butyl peroxy-pivalate (TBPP), a lower temperature peroxide than DTBP. This resulted in a lower viscosity polymer. Further adjustment of the relative concentrations of CCl_4/monomer/initiator resulted in a product of molecular weight 1114 (Run #12). However, this product contained about one Cl_2 per molecule.

Returning tc 180°C and DTBP, the CCl_4/monomer mole ratio was reduced to 0.001 which gave a polymer of 11,000 cps. viscosity and 1009 mol. wt. This product also contained only about one Cl_2 per molecule.

With some idea of the capability of the system, it now seemed reasonable to go to split feeds such that low con-centrations of CCl_4 could be used to obtain the high molecular weight, but that the telogen concentrations could be maintained by injection of more CCl_4 and catalyst midway in the reactor. When the chain transfer constants are much greater than one, additional telogen should be added to supplant CCl_4 already consumed. Such runs are Nos. 16-36, where isooctane solutions of CCl_4 and DTBP were injected midway in the reactor. Mole ratios of CCl_4 to monomer for the secondary feed were based on 98 per cent of monomers fed; two per cent was considered to be converted to polymer. This procedure, however, did not allow us to obtain products of high chlorine functionality. Copolymers having the desired molecular weight had Cl_2 functionalities of slightly less than one. The results are summarized in Table III.

We believe that the source of the difficulty is the higher chain transfer coefficient of CCl_4 at the temperature required for efficient operation of a tubular reactor.

The effect of temperature on transfer activity of CCl_4 may be seen in Figure 1 where the log of the transfer constant* is plotted against the reciprocal of the absolute temperature. Temperatures above 100°C represent maximum internal tube temp-eratures. At 90°C the transfer constants were taken from stirred autoclave data.

* The chain transfer coefficients were calculated from the slopes of straight lines fitted to plots of $1/\overline{DP}_n$ against $[S]/[M]$ as discussed in our last quarterly report. We must re-emphasize that this procedure is purely empirical and gives results which only relate to our particular reaction conditions and comonomer compositions.

TABLE III
TUBULAR REACTOR RUNS - SPLIT FEED
CCl₄ TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

Run No. 24 EMS	16	22	24	28	30	32	36
PRIMARY FEED COMPOSITION							
Neohexene, Wt. %	72.8	72.8	72.8	72.3	72.4	72.6	72.6
Ethylene, Wt. %	26.9	26.9	26.9	26.8	26.8	26.9	26.9
CCl₄, Wt. %	.22	.253	.25	.71	.71	.47	.47
CCl₄, Mole Ratio	.0008	.0009	.0008	.0021	.0021	.0014	.0017
Initiator	DTBP	↑	↑	↑	↑	↑	↑
Initiator, Wt. %	.075	.05	.03	.20	.10	.07	.07
Total feed, gms.	6228	7386	5651	7542	7441	7731	6496
SECONDARY FEED COMPOSITION							
Isooctane, Wt. %	96.5	96.8	97.0	91.7	92.5	94.9	94.9
CCl₄, Wt. %	2.66	2.64	2.64	6.42	6.48	4.42	4.42
CCl₄, Mole Ratio	.0013	.00088	.0008	.0019	.0021	.0012	.0012
Initiator, Wt. %	.887	.559	.30	1.83	.93	.64	.64
Total feed, gms.	770	666	584	722	780	690	477
REACTION CONDITIONS							
Temperature, °C							
Jacket	180	180	182	180	180	180	170
Internal, max.	158	165	160	158	158	158	145
Pressure, mpsi	25±2.5	30±2.5	↑	↑	↑	40±2.5	↑
Operating Time, hrs.	3.2	3.2	2.5	3.6	3.3	3.3	3.2
Nominal Hold-up time, min.	3.11	2.68	2.69	2.91	2.67	2.65	3.04
Number of tubes	4	4	4	4	4	4	4
PRODUCTIVITY							
Yield, gms.	350	282	88	538	381	278	158
% Conversion	5.64	3.83	1.2	7.2	5.2	3.6	2.4
Production rate, gms./hr.	109.4	88.1	35.4	150.8	117.3	83.8	49.9
PHYSICAL PROPERTIES							
Molecular Wt.	976	1019	841	719	651	726	727
Brookfield Visc., cps.	9560	8210	4680	2018	1440	2100	2175
Specific Visc. @ 80°C	.028	.026	.024	.018	.016	.018	.018
Wt. % Cl	5.67	6.67	9.23	11.76	13.86	12.13	13.41
Wt. % O	.52	.55	.37	.73	.41	.26	.25
Description	Yellowish Tan Oil	Tan Oil	Dk. Tan Oil	Yellowish Tan Oil	↑	↑	↑
FUNCTIONALITY							
Cl₂ Per Molecule	.78	.96	1.10	1.19	1.28	1.24	1.38
O₂ Per Molecule	.32	.35	.09	.33	.17	.12	.11

Figure I
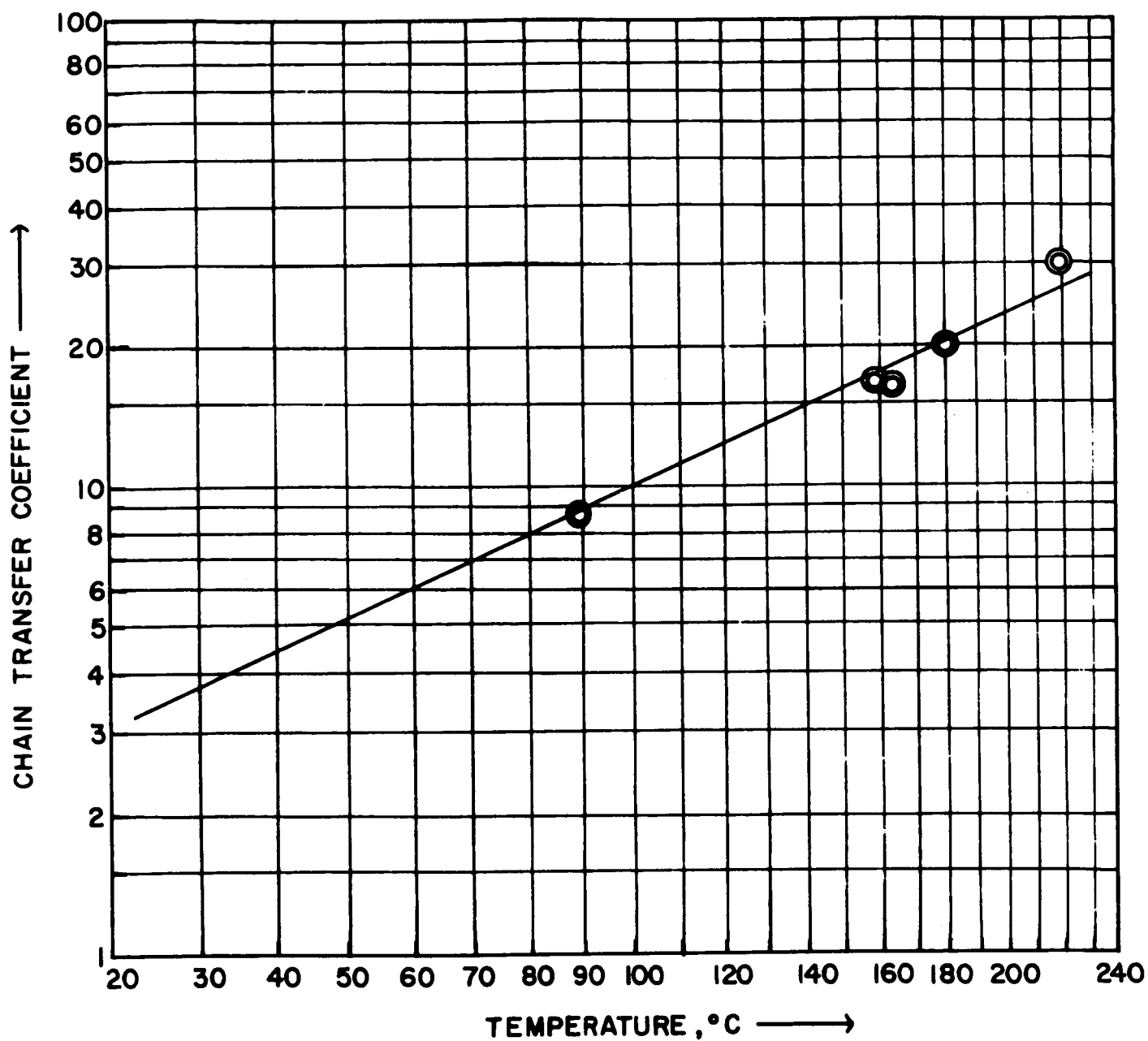
CHAIN TRANSFER COEFFICIENT OF CCl4 AS A FUNCTION
OF TEMPERATURE.

It is probably significant that the tubular reactor product of highest functionality (Run No. 10, 1.61 Cl_2/molecule) was made at very low conversion on both monomers and upon CCl_4. To obtain a thousand molecular weight copolymer the mole ratio of CCl_4 to monomer must be about 0.003 at 90°C and 0.001 at 160°C. At the latter ratio, assuming 100 per cent efficiency on the CCl_4, conversion must be limited to 2.2 per cent on the monomers or non-reactive terminal groups will result. In the higher conversion runs, the CCl_4, is depleted before the polymerization is over, even when split feed is used.

Our results have shown that the continuous tubular reactor is not suitable for preparation of telomers, except in the simple case where the chain transfer coefficient is unity and the telogen/monomer ratio remains constant throughout the the tube. A continuous stirred autoclave reactor is not subject to this difficulty since it operates under steady state conditions. In any future continuous telomerizations, we will use the latter approach rather than the tube. For smaller scale operations, the stirred autoclave reactors with continuous feed of telogen (in order to maintain a constant composition) will be the method of choice.

A discussion of experiments which were performed to convert-Cl and-CCl_3 groups in these telomers to-COOH groups is given in section B.

B.   Reactions of the CCl_4 Telomers

Our experiments have shown that one can obtain telomers of ethylene and neohexene having high chlorine functionalities when CCl_4 is used as telogen under the proper conditions. The functional groups so introduced, however, must be converted into other functional groups which will be useful for low temperature curing reactions if the telomers are to be used as solid propellant binders.

There are two different kinds of functional groups in these telomers. At one end of each molecular is a chloride function, at the other end is a trichloromethyl group:

$$Cl-\overset{\overset{R}{|}}{CH}-CH_2-(\overset{\overset{R}{|}}{CH}-CH_2)_n-\overset{\overset{R}{|}}{CH}-CH_2-CCl_3$$
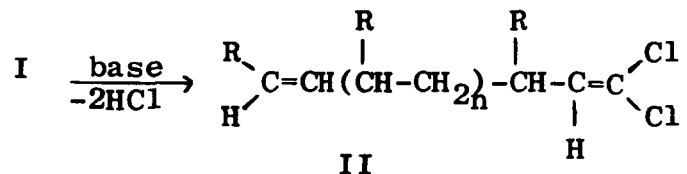
I

R= H or t - butyl
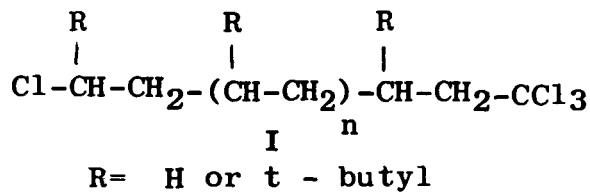
The chemical literature abounds with examples where small molecules containing these functional groups have been converted into carboxylic acids and even di-carboxylic acids.[1-7] Most of these examples have dealt with fairly low molecular weight ethylene telomers containing 1-5 ethylene residues. In these examples, the CCl_3 group has been hydrolyzed to COOH under both acidic and basic conditions. The Cl group has been displaced with CN^-, $S^=$, Br^- and I^-. The products from CN^- displacement have been hydrolysed to give di-carboxylic acids.

With this background, it appeared that the CCl_4 telomers of ethylene and neohexene (described in the last quarterly report, as well as in part A of this report) were very promising intermediates from which curable prepolymers could be produced using standard orgainc reactions.

We have tried the following approaches directed toward placing useful functional groups upon the CCl_4 telomers:

1) Degradation under strongly alkaline conditions, leading to elimination of HCl:

$$I \xrightarrow[-2HCl]{base} \underset{H}{\overset{R}{>}}C=CH(\underset{}{\overset{R}{C}H}-CH_2)_n-\underset{}{\overset{R}{C}H}-\underset{H}{\overset{}{C}}=C\underset{Cl}{\overset{Cl}{<}}$$

II

This could be followed by oxidation of the unsaturated product to a di-carboxylic acid:

$$II \xrightarrow{[O]} \underset{HO}{\overset{O}{>}}C-(\underset{}{\overset{R}{C}H}-CH_2)_n-\underset{}{\overset{R}{C}H}-C\underset{OH}{\overset{O}{<}}$$
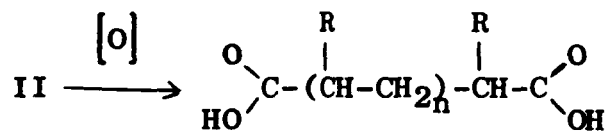
2) Acid hydrolysis of the trichloromethyl group:

$$I + 2H_2O \xrightarrow{H^{\oplus}} Cl-\underset{}{\overset{R}{C}H}-CH_2-(\underset{n}{\overset{R}{C}H}-CH_2)-\underset{}{\overset{R}{C}H}-CH_2-COOH$$
$$+ 3HCl$$
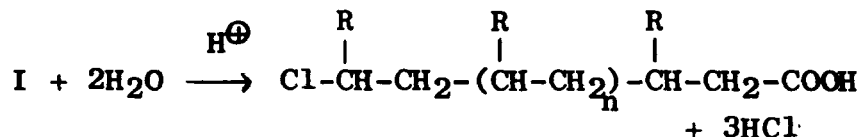
3) Nitrile displacement of chloride, followed by hydrolysis to carboxyl:

$$I \xrightarrow{\text{KCN}} \overset{\displaystyle R}{\underset{\displaystyle |}{N \equiv C-CH-CH_2-(CHR-CH_2)_n-CH}}\overset{\displaystyle R}{\underset{\displaystyle |}{-CH_2-CCl_3}}$$

$$\Big\downarrow H_2O, \ H^+$$

$$\overset{O}{\underset{HO}{\diagdown}}C-\overset{R}{\underset{|}{CH}}-CH_2-(\overset{R}{\underset{|}{CH}}-CH_2)_n-\overset{R}{\underset{|}{CH}}-CH_2-C\overset{O}{\underset{OH}{\diagup}}$$
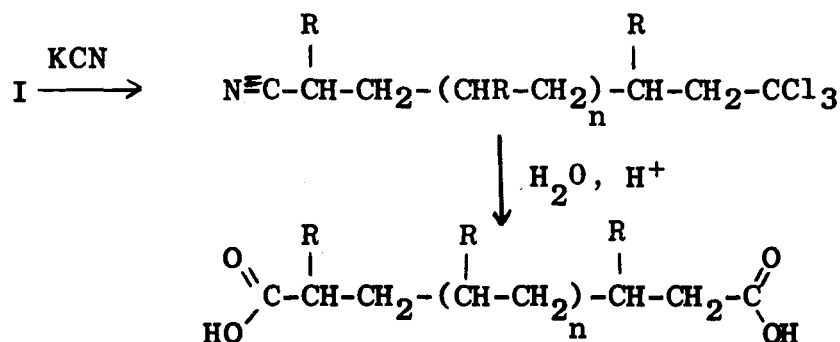
4) Metalation of the terminal alkyl chloride followed by carbonation of the resultant metal alkyl:

$$R\!-\!Cl + 2M \longrightarrow R\!-\!M + M\!-\!Cl$$

$$\Big\downarrow CO_2$$

$$R\!-\!COOH \xleftarrow{H^+} R\!-\!C\overset{O}{\underset{O^{\ominus} \ M^{\oplus}}{\diagup}}$$
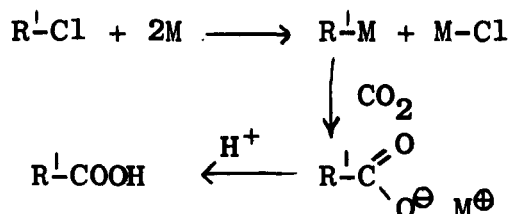
1. Alkaline Degradation

We have used two different sets of conditions under this approach. The first of these is basically similar to the conditions which we had found to be effective in the saponification of C≡N end groups of the AIBN polymers (see Quarterly Report #1 page 9). The CCl_4 telomer is dissolved in butanol and treated with potassium hydroxide in a sealed titanium lined bomb at 250°C under autogenous pressure for about 20 hrs. This procedure was tried on CCl_4 telomers 23-EMS-63, 64 and 65 discussed last quarter. The results are shown in Table IV.

The $-CCl_3$ groups were saponified to $-COO^-$ only to a very minor extent, however a considerable amount of elimination has occurred. This is shown by the presence of unsaturation in the product, as well as by the very low chlorine contents. The strong I.R. bands identified with CCl_3 were absent. The presence of over one oxygen per molecule as well as the 1120 cm^{-1} I.R. band suggest that extensive ether formation has occurred as well. These products are certainly not homogenous by any means, however, the presence of >1 C=C per molecule encouraged us to continue this approach.

TABLE IV

Experiment 8433-No.		3	7-a	7-b	7-c
REACTION CONDITIONS:					
Telomer Used		23-EMS-65	23-EMS-64	23-EMS-63	23-EMS-65
Wt. Telomer, gms.		1.37	20	19	20
Base Used		KOH			
Wt. Base, gms.		10	17.5	20	
Solvent		Butyl Cellosolve		Butanol	
Vol. Solvent, ml		50	100		
Temperature, °C		170	250		
Reaction Time, hrs.		20	20	19	
Yield, gms.		.68	6.38	14.6	12.71
PRODUCT DATA					
Infrared Analysis					
Frequency	Assignment				
700,780 cm^{-1}	-CCl$_3$	Absent	Absent	Absent	Absent
1700 cm^{-1}	-COOH	Absent	Weak	Weak	Weak
972 cm^{-1}	-C=C-	Moderate	Moderate	Moderate	Moderate
1120 cm^{-1}	-C-O-C-	Strong	Moderate	Moderate	Moderate
Mol. Wt.		---	472	610	373
Wt. % O		---	5.38	2.97	5.46
Wt. % Cl		---	.82	0.0	.16
Wt. % C=C		---	6.16	5.4	7.84
Neutralization Equiv.		---	3500	3910	2710
Beilstein Test		+	+	+	-
FUNCTIONALITY					
COOH/Molecule		---	.135	.156	.14
O/Molecule		---	1.59	1.13	1.27
Cl/Molecule		---	.11	0.0	0.0
C=C/Molecule		---	1.2	1.4	1.23

The second procedure we tried under this approach was to treat the telomers with potassium t-butoxide in refluxing tetrahydrofuran. We anticipated these conditions would favor E-1 elimination reactions and lead exclusively to molecules having a double bond at each end. For these experiments we used CCl_4 telomers 23-EMS-126, 24 EMS-6&10, discussed in part A of this report.

When a CCl_4 telomer is added to a refluxing solution of potassium t-butoxide in THF, an immediate exothermic reaction occurs, along with the formation of a white precipitate (presumably KCl since it is water soluble). The reaction is over within one hour. Our preliminary analytical data show that the products isolated from these reactions have no trace of the $-CCl_3$ bonds at 700 and 780 cm^{-1} in their infrared spectra. They all give a strong positive Beilstein test, however, the strong absorption at 970 cm^{-1} (attributed to C=C in the spectra of the KOK/butanol products discussed in the previous section) is not at all evident in the spectra of these products, nor is ether type absorption present either.

We have not received all the analytical data upon these products as yet, and therefore cannot make a definitive appraisal of the results of this approach at this time. Should the analytical data indicate a large proportion of double bonds, we will conduct experiments directed toward oxidation of them to COOH.

2. Acid Hydrolysis

It has been reported that the $-CCl_3$ group is resistant to nucleophilic attack, but is quite susceptible to electrophilic reagents. With this in mind, we have tested the reactivity of the CCl_4 telomers with strong mineral acid.

Treatment of telomer 23-EMS-65 with 48% aqueous HBr at 150°C in a sealed pyrex tube for 20 hours gave essentially no reaction at all.

Friedlina and Vasiléva report[2] that CCl_4 telomers of ethylene are readily attacked by fuming nitric acid to give carboxylic acids. The yields are quite good for low telomers, but decrease with higher telomers.

In our experiments, we have found that the CCl_4 telomers of ethylene and neohexene are rapidly attacked by warm fuming nitric acid. Brown fumes of NO_2 are given off along with HCl gas (the presence of the latter was demonstrated by passing the exit gasses through an $AgNO_3$ solution) from the reaction of the $-CCl_3$ groups.

In a typical experiment, .81g (.0016 moles) of 23-EMS-64 was treated with 10 ml fuming nitric acid and heated for 1 hour in an oil bath at 138°C. When the silver chloride in the trap was collected, dried and weighed, .23g (.0016 moles) was obtained. This corresponds to a 33% conversion of $-CCl_3$ groups.

The product was recovered by diluting with water and extraction with ether. 0.66 gram of a two phase product was recovered after evaporation. 0.48 gram was hexane soluble. This material was a straw colored clear oil. It's I.R. showed about 60% of the original $-CCl_3$ groups remaining. A COOH band of moderate intensity was also present. The hexane insoluble fraction, .14 grams amber oil, contained no $-CCl_3$ functional groups. A very intense $-COOH$ band was present.

The same process was repeated on a larger scale using 18.49g. of 24-EMS-10 and 100 ml fuming nitric acid. The maximum temperature reached was 67°C. Upon work up we obtained 13.23 gms. of a hexane soluble amber oil and 3.17 grams of hexane insoluble, water soluble, viscous amber syrup, containing no $-CCl_3$ groups. The hexane soluble material had a neutralization equivalent of 988. It's I.R. spectrum showed that about 55% of the CCl_3 remained unreacted.

The results of these and other experiments suggest that it will be difficult to obtain a product in which all of the $-CCl_3$ groups have been converted into COOH using this method, and that low yields and considerable by-products are very likely inevitable.

3. CN Displacement

The next group of experiments to be discussed are our attempts to effect a displacement of the terminal chloride in structure I with cyanide ion. Table V summarizes the results of these experiments.

No substitution of CN for Cl occurred in any of the experiments. At 100°C no reaction occurred at all. At higher temperatures, particularly in the very polar solvents DMF and sulfolane, decrease in the amount of $-CCl_3$ groups occurred. This was usually accompanied by the appearance of bands at 970 and 800 cm^{-1} in the infrared spectrum. These probably indicate the formation of double bonds.

TABLE V

Experiment 8433-47 No.	1	2	3	4-a	4-b	5-a	5-b	6-a	6-b	7
Telomer Used	23-EMS-64	47-1	23-EMS-64	←——————— 23-EMS-64 ———————→						
Gms. Telomer	.88	.85	.5	.5	.5	.5	.5	.5	.5	.5
Gms. KCN	2	2	1	--	2	1	1	1	1	1
Gms. KI	--	.1	.05	2	.1	--	--	--	--	--
Solvent	Butyl Cellosolve	Butanol/H$_2$O	Butanol	Butanol/H$_2$O	Butanol/H$_2$O	Sulfolane	DMF	DMF	Sulfolane	DMF
Ml. Solvent	5	10/3	2	2/.5	1/1	2	2	2	2	2
Temp., °C	160	100	200	200	200	200	200	100	100	150
Reaction time, hrs.	20	20	5	2	2	4	4	20	20	12
Vessel Used	Stirred flask	Stirred flask	Sealed Vial, rocked in oil bath ————————————————→							
Result	No reaction at all. No CN in product ————→		No CN in product. CCl$_3$ bands diminished considerably. C=C bands at 970 and 860 in^{-1}			No CN or CCl$_3$ in product. C=C bands at 970 and 860 in^{-1} ————→	No ————→ Reaction			CCl$_3$ bands almost gone. No C≡N band.

4. Metalation

The following experiments were done to test the practicality of this route to carboxyl terminated polymers from the CCl_4 telomers; CCl_4 telomer 23-EMS-128, having $\overline{M}_n$ =587 containing 3.4 Cl per molecule was used in all cases:

1. The telomer was reacted with a 9 fold excess of potassium metal in refluxing tetrahydrofuran. A dark green reaction mixture resulted which gave a strongly positive Gilman test for the presence of organometallics. Dry CO_2 was passed through the reaction mixture until the color was discharged. The mixture was then acidified and worked up to recover the telomer. The product exhibited a strong COOH carbonyl in the infrared, but no trace of the absorption due to the $-CCl_3$ group. The product gave a negative Beilstein test. The neutralization equivalent was 1073.

2. In a similar experiment, CO_2 was passed into the reaction mixture from the beginning. The product resulting had an N.E. of 1273, and a small amount of $-CCl_3$ absorption was still present in the I.R. of the product.

Substituting heptane for THF gave a product with a neutralization equivalent of 2074.

3. In another experiment, addition of CO_2 was delayed until 3 hours after reaction of the telomer with the potassium. At this point the green color had faded and the Gilman test was negative. No COOH groups resulted when CO_2 was added to this reaction mixture. No trace of the CCl_3 absorption could be seen in the I.R. spectrum of the product.

When the above experiments were repeated using lithium dispersion in hexane instead of potassium metal, no carbonation was effected however the $-CCl_3$ groups were no longer present in the products, most of which gave a negative Beilstein test.

We feel that the reason for the failure of the experiments just discussed to introduce carboxyl functionality into the CCl_4 telomers is the instability of the metal alkyls at the temperatures used to form them. An alternate approach, which we plan to pursue is to use metal exchange between the telomers and another organometallic such as t-butyl lithium. This must be carried out at low temperatures. Under these milder conditions, the telomer organometallic compound may survive long enough to be carbonated.
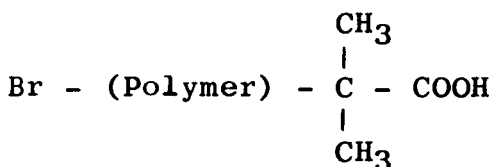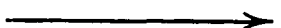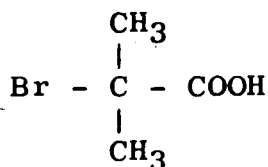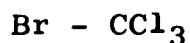
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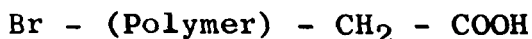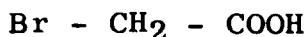
C. New Telogens and Telomers

       In order to circumvent the difficulty we have experienced
in converting the terminal groups of the carbon tetrachloride
telomer into carboxyl groups, we have conducted a series of experi-
ments using other telogens which lead to more reactive telomer end
groups. The telogens tried were: bromotrichloromethane, bromo-
acetic acid, α-bromoisobutyric acid and tert-butyl α-bromoiso-
butyrate. Our experiments have shown that all of these telogens
are more active than carbon tetrachloride. The bromo-ester was
the most active, followed by bromotrichloromethane. Although
more active than carbon tetrachloride, the bromo acids were less
active than bromotrichloromethane. Based upon our previous ex-
perience and published data, we expected the following end groups
to result from these telomerizations:

Telogen   Telomer

$Br - CCl_3 \quad\longrightarrow\quad Br - (Polymer) - CCl_3$

$$Br - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - COOH \quad\longrightarrow\quad Br - (Polymer) - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - COOH$$

(BIBA)

$$Br - CH_2 - COOH \quad\longrightarrow\quad Br - (Polymer) - CH_2 - COOH$$

(BAA)

$$Br - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{/\!/}}{C}\underset{O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3}{\diagdown} \quad\longrightarrow\quad Br - (Polymer) - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{/\!/}}{C}\underset{O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3}{\diagdown}$$
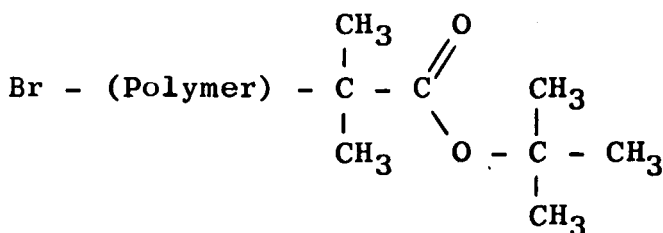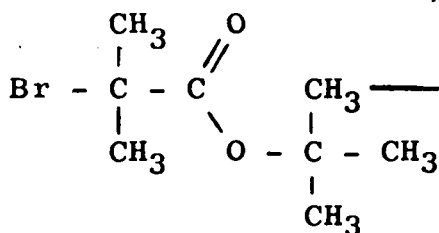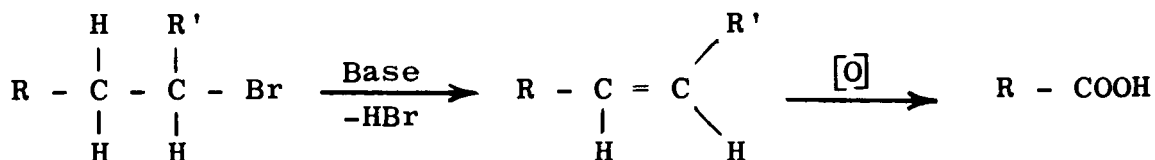
(BBIB)

Bromoacetic acid has hydrogen α- to the carboxyl and could lead to hydrogen terminated products. This is not expected to be as probable as transfer reactions involving the more reactive halogen atom.

We have made telomerization runs in the stirred autoclave reactor using each of these new telogens and have obtained telomers in all cases. The results of these runs are shown in Table VI. The analytical data are incomplete for most of these runs, however the results so far obtained are most encouraging. One product (Run #24-EMS-66) made with t-butyl α-bromo isobutyrate telogen has a molecular weight of 983, contains 3.12% oxygen and 6.86% bromine. These data indicate the presence of 0.95 O_2 per molecule (the ester end groups) and 0.84 bromine atoms per molecule. Another product (Run #24-EMS-62) made with bromoacetic acid telogen has a molecular weight of 934, contains 2.86% oxygen and 4.98 % bromine. These data indicate the presence of 0.84 O_2 per molecule (the ester end groups) and 0.58 bromine atoms per molecule. A higher percentage of nitrogen (.42%) from the initiator in this product corresponds to about .3 nitrogens per molecule. Viscosity data suggests that the other telomers will have similar molecular weights in most cases, and the infrared spectra of the other telomers show intense carboxyl or ester bands.

With the probable exception of the telomers from $BrCCl_3$, these products should be easier to convert to the difunctional carboxyl terminated binder materials than any products we have prepared to date. Having one carboxyl per molecule as a starting point, we can now work upon the more reactive bromine group in any of the following ways for example:

1) Elimination, followed by oxidation:

$$\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{R - C}}}} - \overset{\displaystyle R'}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - Br & \xrightarrow[-HBr]{Base} & R - \overset{|}{\underset{\displaystyle H}{C}} = C\overset{\displaystyle R'}{\underset{\displaystyle H}{{}}} & \xrightarrow{[O]} & R - COOH
\end{array}$$

2) Displacement with Cyanide, followed by hydrolysis:

$$R - Br + CN^{\ominus} \longrightarrow R - CN + Br^-$$
$$\big[H_2O \big] \longrightarrow R - COOH$$
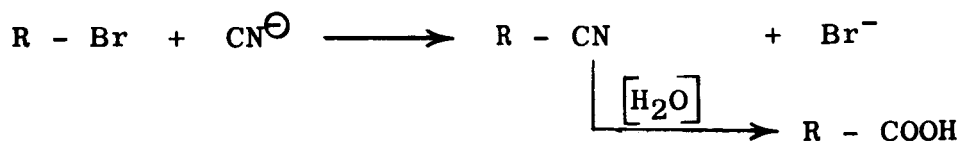
TABLE VI

NEOHEXENE/ETHYLENE TELOMERS

Run No. 24EMS	48	70	49	71	62	69	74	73	66	72
Date 1967	4/3	4/24	4/4	4/25	4/13	4/21	4/28	4/27	4/18	4/26
Initial Charge										
Transfer Agent	CCl₄	CCl₄	BrCCl₃	BrCCl₃	BAA	BIBA	BIBA	BIBA	BBIB	BBIB
" , gms.	0.79	1.59	0.79	2.04	0.88	0.86	0.86	1.72	1.15	2.3
Solvent (φ=benzene)	φ	φ	φ	φ/tBuOH	φ	φ	φ/tBuOH	φ/tBuOH	φ	φ/tBuOH
" , gms.	7.2	7.3	7.3	7.2	7.3	7.3	7.3	7.2	7.3	7.2
Initiator	AIBN	AIBN	AIBN	AIBN	AIBN	AIBN	AIBN	AIBN	AIBN	AIBN
gms.	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066
Neohexene, gms.	689	689	689	685	689	689	689	683	689	683
Ethylene, gms.	260	259	262	256	264	263	255	253	258	259
Fed During Reaction										
Transfer Agent, gms.	7.14	14.3	7.13	18.39	7.9	7.74	7.74	15.5	10.34	20.69
Solvent, gms.	65.4	65.5	65.4	64.9	65.4	65.4	65.4	64.9	65.4	64.9
Catalyst, gms.	0.66	0.60	0.66	0.59	0.66	0.60	0.60	0.59	0.60	0.59
Reaction Conditions										
Temperature, °C	90	90	90	90	90	90	90	90	90	90
Pressure, mpsi Initial	9.0	10.0	9.0	8.2	4.5	10.25	9.5	8.0	9.8	8.5
Final	13.7	15.0	15.0	15.0	17.5	16.25	15.0	15.0	14.8	15.0
Time, Hours	3.67	3.60	3.72	3.58	3.04	3.57	3.58	3.58	2.58	3.67
Productivity										
Yield, gms.	47	57	34	40	15	22	18	22	31	36
Conversion, %	4.96	6.0	3.57	4.25	1.58	2.6	1.91	2.35	3.30	3.82
Rate, %/hr.	1.35	1.7	0.96	1.2	0.52	0.72	0.53	0.66	1.30	1.04
Physical Properties										
Molecular Wgt.			995		934				983	
Brookfield Vis. cps	14,930[21]	3,023[22]	12,000[23]	1,350[22]	-	7,000[21]	-	~3,400[21]	9,710[22]	1,330[21]
Sp. Viscosity @ 80°C.	0.023	0.019	0.028	0.013	0.028	0.028	0.020	0.015	0.024	0.010
Oxygen, wt.%					2.86				3.12	
Chlorine, wt.%			0.0		-				6.86	
Bromine, wt.%					4.98				.0	
Nitrogen, wt.%					.42				.95	
Functionality (O)					.84				-	
(Cl)					.58				.84	
(Br)					.28				.0	
(N)									-	
(COOH)										
Freezing Pt. °C.	-28	-42	-35	-45	-32	-32	-35	-45	-36	-48
Description	dk. tan oil	dk. brown oil	dk. tan oil	dk. brown oil	dk. brown oil	brown oil	brown oil	dk. brown oil	dk. tan oil	dk. tan oil
Meq. Acid/Gm.					0.657	1.86	2.085	2.592		
Max. Stripping Temperature °C. (2-3 MM)	154	170	155	153	126	125	128	128	158	150

3)   Displacement with sulfide, leading to coupling:

$$2 \; R - Br \; + \; S^{\ominus} \qquad\qquad R - S - R \; + \; 2 \; Br^{\ominus}$$

The products from all of the above reactions should contain two carboxyl groups per molecule. Note that reaction 3 leads to a doubling of molecular weight, e.g. the 983 molecular weight product discussed earlier would be converted to a difunctional product, $\overline{M}n \cong 2000$.

We have conducted some experiments using 11-bromo-hendecanoic acid as a model for the bromine terminated telomers discussed earlier:

$$Br - (CH_2)_{10} - COOH$$
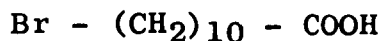
We have found that it dehydrobrominates readily under the action of potassium t-butoxide and is converted to 11-hendecenoic acid.

The bromo acid also reacts rapidly with sodium sulfide to give a new crystalline carboxylic acid in high yield. The new acid contains no halogen and its N.M.R. spectrum is consistent with the structure of the C_{22} sulfide coupling product,
$$HOOC - (CH_2)_{10} - S - (CH_2)_{10} - COOH.$$
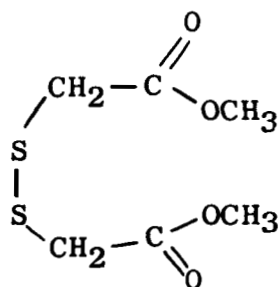
D. Disulfides as Telogens

The use of the disulfides shown below as chain transfer agents in ethylene-neohexene copolymerizations was reported in Quarterly Report No. 5. Table III of that report gave polymerization conditions for runs in which various disulfides were used as telogens. During the last quarter the products from these runs were characterized. The results are listed in Table VII.
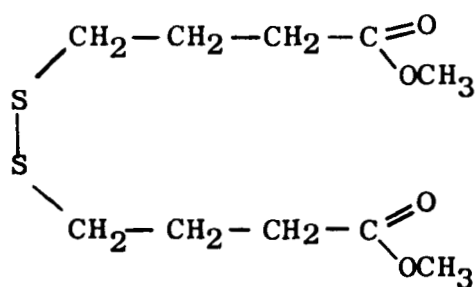
III
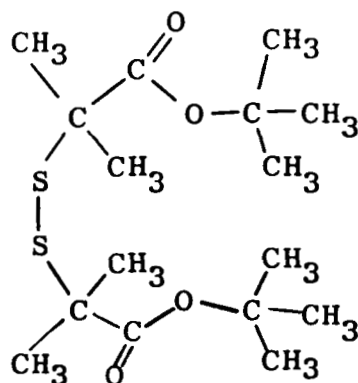
IV

V

TABLE VII

CHARACTERIZATION OF TELOMERS MADE WITH DISULFIDE TELOGENS

Run No. 23 EMS	88	89	91	92	94	101	105	106
Telogen	III	IV	III	III	IV	IV	III	IV
Mol. Wt.	1183	1691	1355	1314	2459	3235	1298	2707
Wt. % Sulfur	2.04	2.30	2.08	4.19	1.89	0.97	2.91	1.19
Wt. % Carbon	80.27	81.24	81.21	-	-	-	-	-
Wt. % Hydrogen	13.52	13.87	13.78	-	-	-	-	-
Wt. % Oxygen	4.44	2.71	2.71	3.91	1.61	0.93	3.03	1.12
Functionality								
O_2 Per Molecule	1.64	1.43	1.15	1.60	1.24	0.94	1.23	0.95
S Per Molecule	.75	1.22	0.88	1.72	1.45	0.98	1.2	1.03

The product from run 88 was hydrolyzed using KOH/butanol under reflux at atmospheric pressure. The resulting prepolymer contained COOH groups as shown by infrared analysis. The following properties were measured: neutralization equivalent weight, 2214; number average molecular weight in THF, 2027; oxygen content, 1.675%. The carboxyl functionality calculated from Mol Wt./N.E was 0.91; calculated from Mol. Wt./O_2 Eq. Wt. was 1.06. From the increase in molecular weight and decrease in O_2 percentage as a result of hydrolysis, it was concluded that product 23 EMS 88 contained some unreacted telogen, which was hydrolyzed and removed during alkaline hydrolysis. Products 91 and 92, made with the same telogen (III), contained unreacted telogen which was verified by comparison with the infrared spectrum of III (dimethyl dithioisobutyrate). It was concluded that III is not active as a transfer agent at 90°C. Run 105 was carried out at 160° which improved the rate of conversion but not the functionality. After alkaline hydrolysis the COOH functionality of 105 was still 1.2.

Runs 89, 94, 101 and 106 were made with telogen IV. Product 89 was chosen for more extensive characterization. One purpose in using the di-tertiary butyl ester of dithioisobutyric acid as a telogen was to facilitate generation of the COOH end group by mild pyrolysis as shown below:
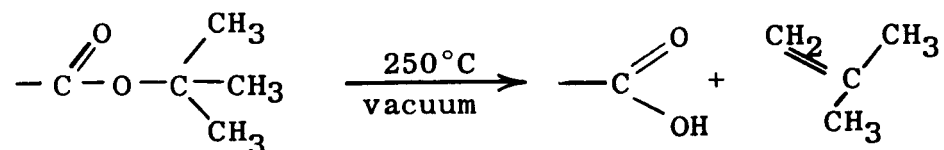
Pyrolysis of product 89 did not result in formation of COOH as had been expected. Instead, volatile material distilled off which had an infrared spectrum identical with that of telogen IV, with the addition of a weak COOH band. Evidently the telogen was slightly pyrolyzed during distillation. The I.R. Spectrum of the residue from the pyrolysis showed only a trace of acid carbonyl, and the ester carboxyl was weaker than that of the starting material. Subsequent additional pyrolysis did not affect this band intensity. Infrared bands of telogen IV were absent in the spectrum of the residue. Analysis of this pyrolyzed product showed that it had a molecular weight of 3850, and contained 0.42 sulfur atoms per molecule and 0.72 O_2 per molecule.

Alkaline hydrolysis of the "pyrolyzed" product gave a material having an N.E. of 11,150, no I.R. ester band and a weak COOH band. If the sulfur functionality previously measured had been on the polymer chain the N.E. after alkaline hydrolysis should have been much smaller. This sulfur must represent residual telogen which was not removed during vacuum pyrolysis, but which was lost during hydrolysis.

These data indicate that sample 89 contained a significant amount of telogen which can be largely removed by vacuum pyrolysis. The ester groups in the product which remained after pyrolysis are not tertiary esters, because of their resistance to pyrolysis. It is concluded that they are derived from the initiator, DMAB.

Samples 94,101 and 106 were not examined in greater detail than described in Table VII.

Several copolymerization runs were also made with dimethyl dithioglycolate (V) as a transfer agent. The polymerization conditions used are given in Table VIII.

The product obtained in run 18 was high in functionality but too low in molecular weight to be of interest as a high energy binder. Some of the molecules were nitrogen terminated from the AIBN initiator used. The products from runs 27, 38 and 68 were higher in molecular weight but were no better than monofunctional. It was concluded that dimethyl dithioglycolate is both a transfer agent and a polymerization retarder. The low functionality indicates that hydrogen transfer is a problem with DMTG. No further work with this telogen is planned.

TABLE VIII

ETHYLENE-NEOHEXENE COPOLYMERIZATIONS WITH DIMETHYL DITHIOGLYCOLATE (DMTG)

Run No. 24 EMS	18	21	27	38	68
Initial Charge					
Solvent	Benzene ⟶				Benzene/ t-butanol
Gms. Solvent	14.8	14.8	14.8	14.8	16.1
Gms. DMTG	0.91	0.91	0.91	0.91	0.81
Neohexene, gms.	570	570	570	570	568
Ethylene, gms.	224	224	210	224	216
Initiator	AIBN	AIBN	AIBN	AIBN	DTBP
Gms., Init.	0.1	0.1	0.2	0.4	0.2
Fed During Run					
Gms., Solvent*	150	150	195	195	145
AIBN, gms.	0.4	.4	1.8	3.6	0.5
DMTG, gms.	8.14	8.14	8.14	8.14	9.27
Reaction Conditions					
Temperature, °C	92	60	90	90	140
Pressure, MPSI					
Initial	2	0.4	0.3	0.1	4.2
Final	15	15	15	15	15
Reaction, Time, hrs.	3.67	5.13	3.67	3.67	2.95
Productivity					
Yield, gms.	7	Trace	12	40	39
Conv., %	0.91	–	1.54	5.13	4.98
Rate, %/hr.	0.25	–	0.42	1.4	1.7
Description	Reddish-Brown Oil	Dis-carded	Clear Oil	Dark Tan Oil	Dark Tan Oil

* Solvent for feed was 1/1 benzene/t-butanol

TABLE IX

CHARACTERIZATION OF COPOLYMERS MADE WITH
DIMETHYLDITHIO-GLYCOLATE

Run No. 24-EMS	18	27	38	68
Molecular Weight	514	988	639	939
Wt. % Sulfur	11.62	1.70	5.49	2.89
Wt. % C	67.5	82.63	76.97	-
Wt. % H	11.11	13.40	12.76	-
Wt. % O	9.47	1.27	4.98	4.01
Wt. % N	1.7	1.07	0.9	-
Functionality				
O_2/molecule	1.52	0.39	.99	1.18
S/molecule	1.86	0.52	1.1	0.85
N/molecule	0.62	0.76	0.41	-

VI. PLANS FOR FUTURE WORK

In the next quarter we will direct our efforts toward obtaining high functionality prepolymers from the new telomers discussed in Part C of this report. We will explore reactions designed to convert the bromide functionality into COOH functionality. We will also investigate coupling reactions in which two or more of the telomer molecules are joined together to give larger molecules with a functionality of two or more. Concurrently, work will be done to improve the efficiency of telomer synthesis and to provide more of these interesting new materials for conversion into curable prepolymers.

VII. NEW TECHNOLOGY

ITEM 1.

U.S. Patent Application #481,907

Applicants: James E. Potts
               Arnold C. Ashcraft, Jr.
               Edgar W. Wise

Title: Propellant Compositions

Date Revealed
to NASA: October 26, 1965

Progress
Reports: See Quarterly Reports
               #1 and #2, Contract
               #951210.

Union Carbide Corporation, on October 10, 1966, granted the National Aeronautics and Space Administration, an agency of the United States of America, an irrevocable, non-exclusive, non-transferable, royalty-free license for the practice of each invention disclosed in the above patent application.

VIII. GLOSSARY

telogen	– a chain transfer agent.
BAA	– bromoacetic acid.
BIBA	– α-bromoisobutyric acid.
BBIB	– tert.-butyl α-bromoisobutyrate.
telomer	– a low molecular weight polymer prepared with the aid of a telogen.
functionality	– average number of functional groups per molecule.
N.E.	– neutralization equivalent, the number of grams of a substance which is neutralized by one equivalent of base.
DMAB	– dimethyl α,α'-azobis [isobutyrate.]
AIBN	– α,α'-azobis [isobutyronitrile.]
DMTG	– dimethyl dithioglycolate.
DTBP	– di-tert.-butyl peroxide.
TBPP	– tert.-butyl peroxypivalate.
Beilstein test	– a flame test for halogen.
Gilman test	– a color test for organometallics.
sulfolane	– tetramethylene sulfone
THF	– tetrahydrofuran
DMF	– dimethyl formamide.
N.M.R.	– nuclear magnetic resonance
I.R.	– infrared

JEP/ACA:bjc:pdl:lvm